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Research Article

Removal of Pb(II) Ions in Fixed-Bed Column from Electroplating Wastewater of Bursa, an Industrial City in Turkey

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Removal of Pb(II) ions from electroplating wastewater of Bursa, an industrial city in Turkey, was investigated in fixed-bed column. The experiments were conducted to study the effect of important design parameters such as column bed height and flow rate. The breakthrough profiles were obtained in these studies. At a bed height of 14 cm and flow rate of 6 mL/min, the metal-uptake capacity of poly(ethylene glycol dimethacrylate-1-vinylimidazole) [poly(EGDMA-VIM)] beads for Pb(II) ions was found to be 90 mg/g. Bed Depth Service Time (BDST) model was used to analyse the experimental data and evaluate the performance of adsorption column. For various flow rates, adsorption capacity per unit bed volume (N_0) and adsorption rate constant (k_a) are in the range of 2370–3560 mg/mL and 0.0225–0.0616 L/mg h, respectively. The saturated column was easily regenerated by 0.1 M HNO_3 and the poly(EGDMA-VIM) beads in fixed-bed column could be reused for Pb(II) ions removal.

1. Introduction

Removing heavy metal ions from wastewater due to its supreme toxicity is a specific concern. The ions are highly toxic pollutants generated from many industrial processes such as mining, chemicals manufacture, electroplating, distilling, and brewing [1]. Pb(II) ions are hazardous because it could lead to a wide range of spectrum health problems, such as nausea, convulsions, coma, renal failure, cancer, and subtle effects on metabolism and intelligence [2].

Many methods have been used for the removal of Pb(II) ions from aqueous solutions, including chemical precipitation, chemical oxidation and reduction, ion exchange, filtration, electrochemical treatment, and evaporative recovery. However, these high-technology processes have significant disadvantages, including incomplete metal removal, requirements for expensive equipment and monitoring systems, high reagent or energy requirements, or generation of toxic sludge or other waste products that require disposal [3]. In the past few decades, adsorption is considered a powerful technique that was extensively used for removal of heavy metal ions from domestic and industrial effluents [4]. Polymeric adsorbents are generally preferred for the removal of heavymetal ions due to their high efficiency, easy handling, availability of different adsorbents, reusability, and cost effectiveness. Toxic metal-ion removal with chelating polymers would be of great importance in environmental applications [5, 6]. For industrial wastewater treatment, adsorption in fixed-bed column is preferable [7]. Therefore, experimental data obtained from the laboratory scale fixed-bed column are helpful in designing an adsorption column for industrial application.

The aim of this work is to remove Pb(II) ions from electroplating wastewater using fixed-bed column. The important design parameters such as column bed height and flow rate have been investigated. The breakthrough profile for the adsorption of Pb(II) ions was analysed using the Bed Depth Service Time (BDST) model. In addition, the removal capacity of Pb(II) ions in electroplating effluent for the adsorption-desorption cycles has also been investigated.

2. Experimental

2.1. Materials and Methods. Ethylene glycol dimethacrylate (EGDMA) was obtained from Merck (Darmstadt, Germany), purified by passing through active alumina and stored at 4°C until use. N-Vinylimidazole (VIM, Aldrich, Steinheim, Germany) was distilled under vacuum (74–76°C, 10 mm Hg). 2,2′-Azobisisobutyronitrile (AIBN) was obtained from Fluka A.G. (Buchs, Switzerland). Poly(vinyl alcohol) (PVAL; Mw: 100.000, 98% hydrolyzed) was supplied from Aldrich Chem. Co. (USA). All other chemicals were of reagent grade and were purchased from Merck AG (Darmstadt, Germany). All water used in the chelation experiments were purified using a Barnstead (Dubuque, IA, USA) ROpure LP reverse osmosis unit with a high flow cellulose acetate membrane (Barnstead D2731) followed by a Barnstead D3804 NANO pure organic/colloid removal and ion exchange packed-bed system.

2.2. Preparation of Poly(EGDMA-VIM) Beads. The poly(EGDMA-VIM) beads were selected for the synthesis of metal-chelate affinity adsorbent for Pb(II) adsorption. The poly(EGDMA-VIM) beads were produced by suspension polymerization in an aqueous medium as described in our previous article [8]. EGDMA and VIM were polymerized in suspension by using AIBN and poly(vinyl alcohol) as initiator and stabilizer, respectively. Toluene was used as diluent (as a pore former). A typical preparation procedure was exemplified below. Continuous medium was prepared by dissolving poly(vinyl alcohol) (200 mg) in purified water (50 mL). For the preparation of the dispersion phase, EGDMA (6 mL; 30 mmol) and toluene (4 mL) were stirred magnetically at 250 rpm for 15 min at room temperature. Then, VIM (3 mL; 30 mmol) and AIBN (100 mg) were dissolved in the homogeneous organic phase. The organic phase was dispersed in the aqueous medium by stirring the mixture magnetically (400 rpm), in a sealed-pyrex polymerization reactor. The reactor content was heated to 70°C within 4 h, and the polymerization was performed at 90°C for 2 h at 600 rpm. Final beads were extensively washed with ethanol and water to remove any unreacted monomer or diluent and then stored in distilled water at 4°C. FTIR was undertaken to determine the composition of poly(EGDMA-VIM) beads. The FTIR spectrum of poly(EGDMA-VIM) with characteristic peaks appears at 3120 cm^{-1} (characteristic imidazole ring, C=C–H/N=C–H), 1500 cm^{-1} (C–C/N–C stretching), 1220 cm^{-1} (ring vibration) and 1098 cm^{-1} (in-plane ring C–H bending). The carbonyl peak appears at 1720 cm^{-1}, and the peak at 1150 cm^{-1} is associated with the C–O vibration of EGDMA. These data confirmed that the poly(EGDMA-VIM) beads were formed with functional groups VIM. Figure 1 shows SEM micrographs of poly(EGDMA-VIM) beads.

2.3. Wastewater. Composite electroplating wastewater was collected from the discharge point of the electroplating industry located in Bursa City, Turkey, during October 2008. Wastewater was filtered through a qualitative filter paper and stored at 5°C for further use. The characteristics of the wastewater after filtration are presented in Table 1.

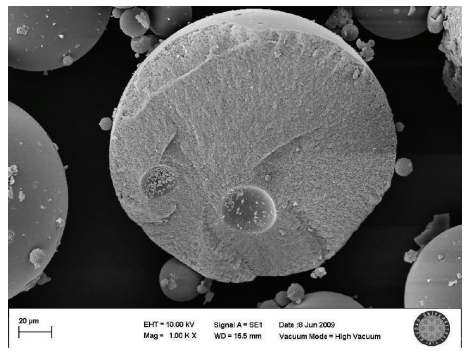

Figure 1: SEM micrographs of poly(EGDMA-VIM) beads.

Table 1: Wastewater characteristics.

Parameter	
pH	9.4
TSS[a], mg/L	153
TDS, mg/L	3552
Conductivity, μS/cm	7324
Sulphate, mg/L	284
Chloride, mg/L	625
Pb, mg/L	11.9

[a]Before filtration.

Total suspended solids (TSS), total dissolved solids (TDS), chloride (Cl^-), and sulphate (SO_4^{-2}) were analysed using standard methods [9]. The pH and conductivity values were measured with a pH meter (Sartorius, Model PB-11, Germany) and a WTW 315I conductivity meter (WTW, Germany), respectively. Atomic absorption spectrometry (ATI Unicam, Model 929, USA) was applied to investigate the concentration of lead.

2.4. Adsorption-Desorption in Fixed-Bed Column. Adsorption in a continuous-flow system was performed using a fixed bed column reactor (2.0 cm i.d., 45 cm column length). A glass filter (disc por.4) was introduced at the bottom of the column. Column studies were conducted using a downflow technique. The schematic diagram of the fixed bed column is shown in Figure 2.

Wastewater pumped through a column using a peristaltic pump (Heidolph, Germany). Samples were collected after filtration at different time intervals and analyzed for lead. Operation of the column was stopped when the effluent Pb(II) ion concentration exceeded a value of 11.3 mg/L (i.e., 95% breakthrough using initial concentration of 11.9 mg/L). Desorption was carried out by passing 0.1 M HNO_3 through the column bed at a flow rate of 6 mL/min. On the completion of desorption cycle, the column was rinsed with deionised water in the same manner as for adsorption until a pH value of 7 was observed. The desorbed and regenerated column bed was reused the next cycle.

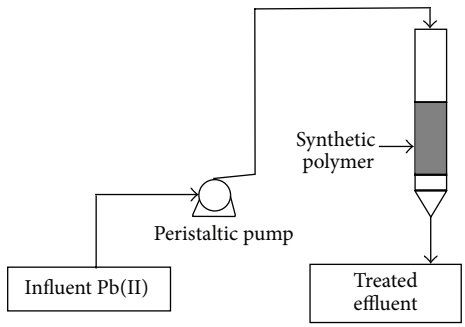

Figure 2: Schematic diagram of laboratory-based small column for fixed bed studies.

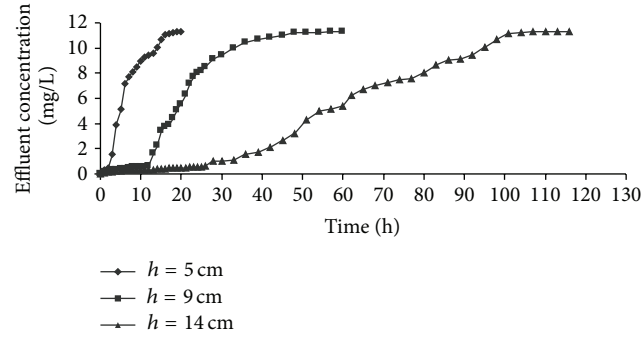

Figure 3: Effect of bed height on the breakthrough curves for adsorption of lead (flow rate = 6 mL/min; initial Pb(II) conc. 11.9 mg/L).

2.5. Modeling and Analysis of Column Data. The performance of packed bed is described through the concept of the breakthrough curve. Both the time until the sorbed species are detected in the column effluent (breakthrough point) at a given concentration, and the shape of the concentration-time profile or breakthrough curve are important characteristics for operation, dynamic response, and process design of a sorption column because they directly affect the feasibility and economics of the sorption phenomena. Experimental determination of these parameters is very dependent on column operating conditions such as feed pollutant concentration and flow rate. A breakthrough curve is usually expressed in terms of adsorbed pollutant concentration (C_{ad} = inlet pollutant concentration (C_0)-outlet pollutant concentration (C_b)) or normalized concentration defined as the ratio of effluent pollutant concentration to inlet pollutant concentration (C_b/C_0) as a function of flow time (t) or volume of effluent (V_{eff}) for a given bed height [10].

Effluent volume (V_{eff}) is calculated

$$V_{eff} = Ft_{total}, \tag{1}$$

where t_{total} and F are the total flow time and volumetric flow rate. The quantity of metal retained in the column represented by the area above the breakthrough curve (C versus t) is obtained through numerical integration [11].

The breakthrough time (t_b, the time at which metal concentration in the effluent reached 0.6 mg/L) and bed exhaustion time (t_e, the time at which metal concentration in the effluent exceeded 11. 3 mg/L) were used to evaluate the mass transfer zone (Δt) given by

$$\Delta t = t_e - t_b. \tag{2}$$

Total amount of metal to the column (m_{total}) can be calculated from

$$m_{total} = C_0 F t_e. \tag{3}$$

A number of mathematical models have been developed for the use in design of column parameters. Among various models, the model proposed by Bohart and Adams [12] is widely used [13, 14]. The simplified equation of Bohart and Adams model is as follows:

$$t = \frac{N_0}{C_0 v} Z - \frac{1}{k_a C_0} \ln\left(\frac{C_0}{C_b} - 1\right), \tag{4}$$

where C_0 is the initial metal ion concentration (mg/L); C_b is the breakthrough metal ion concentration (mg/L); N_0 is the sorption capacity of bed (mg/L); v is the linear velocity (cm/h); and k_a is the rate constant (L/mg h). Equation (4) can be used to determine the service time (t) of a column of bed height Z, given the values of N_0, C_0, and k_a which must be determined for laboratory columns operated over a range of velocity values, V.

3. Results and Discussion

Investigations of removal studies in the fixed-bed column with poly(EGDMA-VIM) beads were performed by varying flow rate from 6 to 10 mL/min for initial Pb(II) concentration of 11.9 mg/L at pH 9.4. Bed height of 5 cm at which the polymer beads showed saturation at a very early stage compared to other bed heights. The uptake of lead increased by increasing the bed height from 5 to 14 cm. This was reflected from the breakthrough with a bed height of 5 cm at which the polymer beads showed saturation at a very early stage compared to other bed heights. The increase in the metal-uptake capacity with the increase of bed height in the column was due to the increase in the surface area on adsorbent which provided more binding site for the adsorption. The breakthrough time was also increased with an increase in bed height (Figure 3) [11, 15].

Figure 4 represents the effect on the breakthrough curves when changing the flow rate from 6 to 10 mL/min.

In general, sharper breakthrough curves were obtained at higher flow rates. The breakpoint time and total adsorbed lead quantity also decreased with increasing flow rate. This behavior can be explained by the fact that lead adsorption is affected by insufficient residence time of the solute in the column. The insufficient time decreases solute in the column, that is, the bonding capacity of the Pb ions with the imidazole groups present in the poly(EGDMA-VIM). The sorption data were evaluated, and the total sorbed quantities, maximum lead uptakes with respect to flow rate, are presented in Table 2. It is also observed that a maximum lead uptake of 90 mg/g was observed at 6 mL/min.

Table 2: Column data and parameters obtained for poly(EGDMA-VIM).

Bed height (cm)	Flow rate (mL/min)	Uptake (mg/g)	t_b (h)	t_e (h)	Δt (h)	(dC/dt)[b] (mg/L h)
5	6	44.3	2.6	18.5	15.9	0.67
	8	37.8	2.3	11.8	9.5	1.12
	10	35.1	1.6	8.8	7.2	1.48
9	6	65.4	11.5	48.9	37.4	0.29
	8	53.7	9.2	30.1	20.9	0.51
	10	49.1	4.6	22.0	17.4	0.61
14	6	90.0	26.0	105.1	79.1	0.13
	8	78.3	20.2	68.3	48.1	0.22
	10	72.5	10.9	50.4	39.5	0.27

[a]Conditions: initial Pb (II) conc. 11.9 mg/L.
[b]Slope of the breakthrough curve from t_b to t_e.

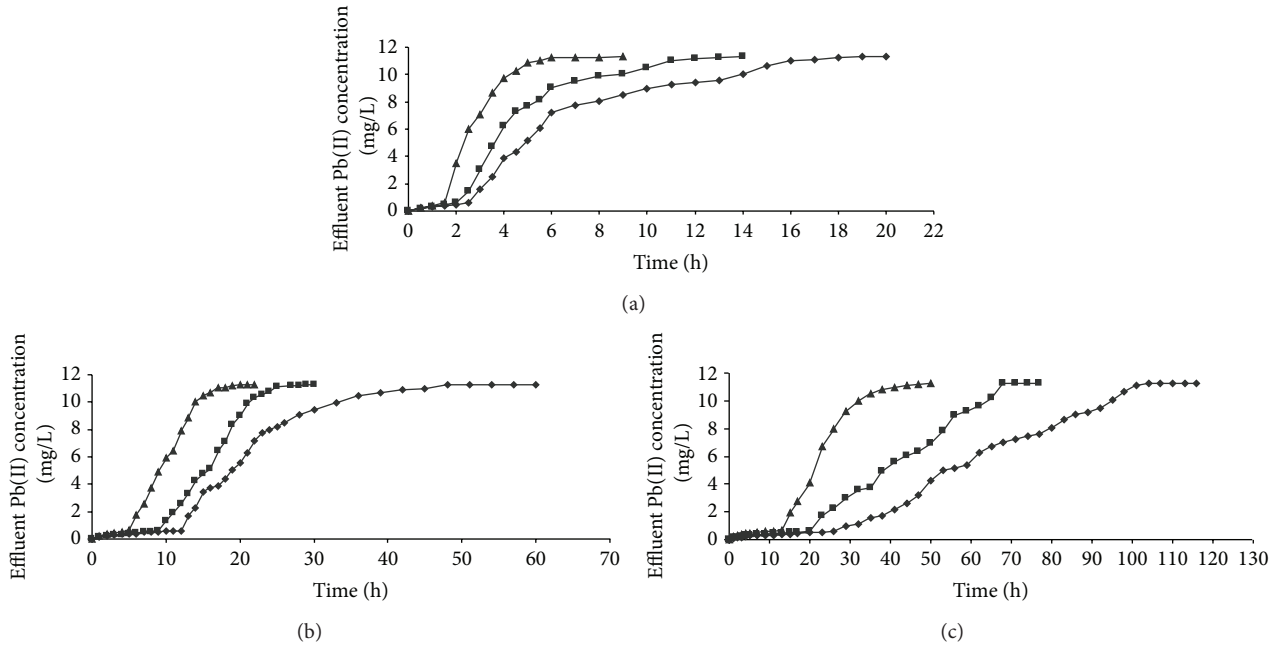

Figure 4: Breakthrough curves at different flow rates obtained for [poly(EGDMA-VIM)]. (a) Bed height 5 cm, (b) bed height 9 cm, and (c) bed height 14 cm. Conditions: initial Pb(II) conc. = 11.9 mg/L; pH 9.4 flow rate: (♦) 6 mL/min; (■) 8 mL/min; (▲) 10 mL/min.

The Bed Depth Service Time (BDST) is expressed in the Bohart-Adams equation as

$$t_b = a \cdot Z + b, \tag{5}$$

where

$$a = \text{slope} = \frac{N_0}{C_0 V},$$
$$b = \text{intercept} = \frac{1}{k_a C_0} \ln\left(\frac{C_0}{C_b} - 1\right), \tag{6}$$

where t_b is the time at which the metal concentration in the effluent reached 0.6 mg/L(h) and Z is the bed height (cm). The parameters N_0 and k_a are calculated from the slope of the linear plot of t_b versus Z. Comparison of experimental and predicted service times for various volumetric flow rates (6, 8, and 10 mL/min) and constant lead concentration (11.9 mg/L) on BDST model is shown in Figure 5. The calculated service times for various flow rates have agreed well with the experimental data.

The critical bed depth (Z_0), the adsorption capacity (N_0), and the rate constant (k_a) were calculated. The data is shown in Table 3.

However, k_a has shown a consistent trend for variation of flow rates which is not the case for N_0. For various flow rates, the values of N_0 and k_a are in the range of 2370–3560 mg/mL and 0.0225–0.0616 L/mg h, respectively. The similar trend was observed by Walker and Weatherley [16] and Kumar et al. [17].

3.1. Regeneration. Once the adsorbent poly(EGDMA-VIM) was saturated with lead ions, it was important to regenerate the polymer for the recovery of lead ions as well as the use

Table 3: Effect of flow rate on BDST model.

Flow rate (mL/min)	v (cm/h)	N_0 (10^3 mg/L)	k_a (L/mg h)	Z_0 (cm)	r^2
6	114.7	3.56	0.0225	4.2	0.995
8	152.8	3.63	0.0307	4.1	0.996
10	191.1	2.37	0.0616	3.9	0.981

Conditions: C_0 = 11.9 mg/L.

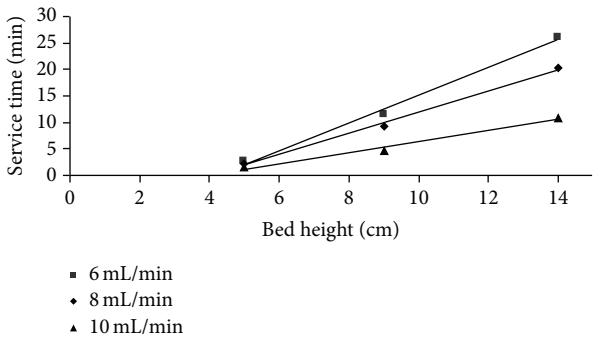

Figure 5: BDST plots for various flow rates for poly(EGDMA-VIM). Conditions: C_0 11.9 mg L^{-1}; (■) 6 mL/min experimental; (♦) 8 mL/min experimental; (▲) 10 mL/min experimental; (—) calculated.

of poly(EGDMA-VIM) for adsorption. The desorption of the column was carried out by passing to regenerate poly(EGDMA-VIM) in order to recover the metal. Firstly, 5 cm depth of poly(EGDMA-VIM) was saturated by influent solution of 11.9 mg/L initial Pb(II) concentration at the flow rate of 6 mL/min. Then the exhausted poly(EGDMA-VIM) was regenerated using 0.1 M HNO_3 solution at the same flow rate. Next, the column was washed with distilled water. In this paper, we repeated the above process three times. Consecutive desorption and sorption cycles indicated that Pb(II) was easily desorbed. The removal capacity of poly(EGDMA-VIM) decreased at a certain extent in the second cycle, but there was no obvious change in the third cycle which decreased by not more than 5%. Hence, it was proved that the regeneration and reuse of poly(EGDMA-VIM) were an economical and efficient method for removal of Pb(II) from Pb(II)-rich electroplating wastewater streams.

4. Conclusions

In this study, it was determined that poly(EGDMA-VIM) beads could be utilized as an effective adsorbent for the removal of Pb(II) from rich electroplating wastewater streams. The adsorption of Pb(II) was strongly dependent on the bed depth and flow rate. The increase in bed height and decrease in flow rate resulted in improved sorption performance. The BDST model constants were determined and proposed for the use in column design. Poly(EGDMA-VIM) can be regenerated efficiently and used again for a number of times. The regeneration and subsequent use of poly(EGDMA-VTAZ) show that the adsorption process can be applied using column operation. This will enhance its option to be economical for the removal of Pb(II) using poly(EGDMA-VTAZ).

Nomenclature

C_{ad}:	Adsorbed pollutant concentration (mg/L)
C_0:	Inlet Pb(II) ions concentration (mg/L)
C_b:	Outlet Pb(II) ions concentration (mg/L)
F:	Volumetric flow rate (L/h)
k_a:	Bed depth service model rate constant (L/mg h)
m_{total}:	Total amount of Pb(II) ions sent to column (g)
N_0:	Sorption capacity of bed (mg/L)
Poly(EGDMA-VIM):	Poly(ethylene glycol dimethacrylate-1-vinylimidazole)
t:	Service time (h)
t_b:	Time at which Pb(II) ions concentration in the effluent reached 0.6 mg/L (h)
t_e:	Time at which Pb(II) ions concentration in the effluent reached 11.3 mg/L (h)
Δt:	Mass transfer zone (h)
t_{total}:	Total flow time (h)
TSS:	Total suspended solids (mg/L)
TDS:	Total dissolved solids (mg/L)
V_{eff}:	Volume of the effluent (mL)
v:	Linear flow rate (cm/h)
V:	Throughput volume (L)
Z:	Bed height (cm).

Conflict of Interests

The authors do not have a direct financial relation with the commercial identities mentioned in this paper that might lead to a conflict of interests for any of the authors.

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